INTERLABORATORY
STUDY 93-1
JULY 1993

TRACE
METAL
STANDARD
SOLUTIONS

IN SUPPORT OF

THE INTEGRATED
ATMOSPHERIC
DEPOSITION
NETWORK
(IADN)

JUNE 1994

Environment   Environnement
Canada   Canada

Atmospheric   Service
Environment   de l'environnement
Service   atmosphérique

⊗ Ontario

INTERLABORATORY STUDY 93-1

TRACE METAL STANDARD SOLUTIONS

IN SUPPORT OF

THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

JULY 1993

Report Prepared by

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for

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Laboratory Services Branch
Ontario Ministry of Environment and Energy
PIBS No. 3100

and

Air Quality Research Branch
Atmospheric Environment Service
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TABLE OF CONTENTS

1   SUMMARY OF INTERLABORATORY STUDY 93-1

Interlaboratory Study 93-1 was the second study for Trace Metals analysis initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an assessment of between-laboratory variability. Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Six participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 8 different elements. Results were received from all participating laboratories.

The results of this interlaboratory study indicate that the participants have maintained or improved their between-laboratory variability as compared to the first interlaboratory study[4] among this group of laboratories. Individual participants may have problems with one or two of the Trace Metals, but to maintain confidentiality, individual laboratories' performance has not been directly compared for the two studies.

The target levels were lower in this study as compared to the previous study[4], so as to evaluate sensitivity at lower levels. Intercept problems were demonstrated for Aluminum, Copper, Lead, and Zinc. Improvements may not be possible due to the current state of analytical capability.

It is the intent that future interlaboratory studies will continue to monitor performance among this group of laboratories, and will attempt to include precipitation and ambient air samples as part of these studies.

2   INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems, as well as ensuring data quality. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was the second in a series designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[2]. This interlaboratory study provides information to help establish the comparability of data sets and is a recommended activity of the IADN Quality Assurance Program Plan[3]. Sponsorship of this interlaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Co-ordination of the study was done by the Atmospheric Environment Service (AES) of Environment Canada and preparation of all materials was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interlaboratory Study 93-1 targets laboratories analyzing for Trace Metals in ambient air and/or precipitation. The aim of this study was to continue to monitor the comparability of instrumental calibration among the participating laboratories. The first study in this series was conducted in 1992[4]. Each participant received a set of 4 ampouled standards containing eight different elements (Trace Metals) ready for direct instrumental analysis.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3   PROCEDURE

3.1   Preparation of Ampouled Standards

The QMU of LSB, MOEE provided individual concentrated stock solutions of the eight Trace Metals to be used in this study. These solutions had been previously verified against US-EPA materials and used extensively for LSB in-house Performance Evaluation samples and MOEE interlaboratory studies. Four combined solutions were prepared by diluting aliquots of the concentrated stocks in distilled, deionized water (DDW). Target levels attempted to cover the routine analytical range of most participants. The solutions were preserved with 2% concentrated nitric acid. The solutions were sealed into 50 mL clear ampoules that had been cleaned and then leached overnight with 5% nitric acid.

The ampouled solutions were stored at room temperature until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on July 14, 1993. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the samples using their routine in-house methods used to analyze ambient air or precipitation samples for the IADN program. The solutions were intended for direct instrumental analysis and participants were told not to use any digestion or pre-concentration procedures. Participants were requested on the report form provided (Appendix 2) to indicate the Instrument used and any dilution factors (if necessary). All participants were assigned a unique identification code.

3.4 Data Reporting

Results were submitted to AES in written form. All data were manually entered by laboratory code into an electronic spreadsheet.

The participating laboratories were mailed a copy of the tables of results on October 4, 1993. No corrections were reported.

The interlaboratory mean, median, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each element and are included in Table 1, Appendix 1. As the data set is small, these calculated values are provided as an approximate indicator of the spread of the data, and may not necessarily be statistically correct. A list of the instrumentation used by the participants is provided in Table 2.

To easily compare the performance of the participating laboratories, the difference from target for each participant for each solution was plotted for each Trace Metal. The percent difference from target for each Trace Metal was plotted in a similar manner. These graphs are included in Appendix 1.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

Results were received from all of the laboratories which received the ampouled standards. A description of the principles upon which the following discussion is based is provided in Appendix 3.

The results for Aluminum (Figure 1) demonstrate agreement among four of the participants. Laboratory 9311 has a large negative slope and small negative intercept bias, and Laboratory 9316 is erratic (see individual discussion below). The other four participants demonstrate an intercept bias of approximately 20 μg/L, which is consistent with the first interlaboratory study among these participants[4]. As noted in

the first study, the analytical techniques currently available are not as sensitive for Aluminum as compared to other Trace Metals, so that the level of performance demonstrated at the lowest concentration in this study appears to be what is currently achievable. Excluding Laboratories 9311 and 9316, the remaining participants (9312, 9313, 9314 and 9315) demonstrate a between-laboratory range of 30% at the higher concentrations (Figure 2), which is an improvement from the first study (between laboratory range of 40%)[4].

The Arsenic results (Figure 3) demonstrate moderate between-laboratory slope-dependant bias. The between-laboratory range is 15-20% (Figure 4), which is an improvement from the first study (between-laboratory range of 20-30%)[4].

The Cadmium results (Figure 5) demonstrate good agreement among the participants, except for Laboratory 9311 in Ampoules IADN3 and IADN4. Laboratory 9315 has a slight positive slope bias in Ampoule IADN4. Except for Ampoule IADN2, the between-laboratory range is 10-15% (Figure 6), excluding Laboratory 9311. These participants are maintaining the same high level of agreement demonstrated in Interlaboratory Study 92-4[4].

Except for Laboratory 9312, the other laboratories demonstrate an intercept bias of approximately 0.3-0.5 μg/L for Chromium (Figure 7). This is an improvement from Interlaboratory Study 92-4, which had an intercept bias of 2-5 μg/L[4]. Laboratory 9312 has a slight positive slope bias for Chromium at higher concentrations, compared to the other participants, and their performance was also somewhat erratic. Between-laboratory performance is variable at the lower concentrations, but improves at the highest concentration level (IADN4) in this study (Figure 8). The between-laboratory range at the high concentration is at the same level (25%) as in the first study[4].

The results for Copper (Figure 9) demonstrate an intercept bias of approximately 1 μg/L, except for Laboratory 9312 who was biased high. The between-laboratory range is approximately 20% (Figure 10), excluding Laboratories 9311 and 9312 in IADN1. Both the range and intercept have improved compared to the first interlaboratory study (range of 30% and intercept of 3-5 μg/L)[4].

The Lead results (Figure 11) demonstrate good agreement among four of the participants. Laboratory 9312 has a marked negative slope problem, resulting in a low bias at the higher concentrations. Laboratory 9311 has a slight negative slope and is also biased low compared to the other participants. Excluding Laboratory 9311, the other participants demonstrate an intercept of approximately 1 μg/L, which is an improvement from the first interlaboratory study (intercept of 2 μg/L)[4]. The between-laboratory range among Laboratories 9313, 9314, 9315 and 9316 for the higher concentrations is approximately 10% (Figure 12), an improvement from 20% in Interlaboratory Study 92-4[4].

Only three participants reported results for Selenium. Laboratories 9312 and 9314 demonstrate good agreement with each other and with the target (Figure 13). They do not demonstrate any slope or intercept biases. Laboratory 9315 has a large negative slope bias compared to the other participants, though they are within approximately 10% of the target (Figure 14) for all but Ampoule IADN2.

All of the participants demonstrated a high intercept bias for Zinc (Figure 15). As with Aluminum, it appears that the analytical techniques are not sensitive enough for the low levels of Zinc used in this study. Laboratory 9316 has a high positive slope bias and Laboratory 9311 has a large negative slope bias (Figure 15). The agreement

among the other participants (9312, 9313, 9314 and 9315) at the higher concentrations is in a range of approximately 15%, which is an improvement from Interlaboratory Study 92-4 (between-laboratory range of 25%)[4].

The overall performance indicates that the between-laboratory variability for four of the participants for most Trace Metals is within ±5-8% over the concentration range of this study. Some Trace Metals (Aluminum, Chromium and Copper) have higher between-laboratory variability (±10-15%). However the between-laboratory range has improved (i.e. is smaller) for all Trace Metals, compared to the first interlaboratory study[4] between these participants.

The target levels were lower in this study than in the previous study[4], so as to further assess intercept biases. While the intercept biases appears to have improved for some Trace Metals (Chromium, Copper, and Lead), several of the participants have intercept problems for many of the Trace Metals. For Aluminum and Zinc, the results indicate that the available analytical techniques are not sensitive enough to lower the intercepts of 20 μg/L and 5 μg/L, respectively.

INDIVIDUAL LABORATORY PERFORMANCE

While most of the participants in this study are the same laboratories that participated in Interlaboratory Study 92-4[4], the laboratories have been assigned different ID Codes in this study. Therefore the following individual laboratory review is based only on the results of this study, with no comparisons to previous studies, so as to maintain laboratory confidentiality.

Laboratory 9311

Laboratory 9311 had problems with their hydride generator and were unable to report results for Arsenic and Selenium.

This laboratory had a negative slope problem for all the Trace Metals except Chromium and Lead. Except for Chromium, they were also biased low relative to the target and to the other participants in the two higher concentration ampoules (IADN3 and IADN4), emphasizing their negative slope problems. For several Trace Metals (Cadmium, Copper, and Zinc), Laboratory 9311 had a high intercept. For Lead they had a negative intercept. Comparison of their standards with reference standards over the full calibration range should help to reduce these problems.

Laboratory 9312

Laboratory 9312 used two different instruments for this study. For Aluminum and Zinc they used ICP-AES (Table 2). They had very good agreement with the target and interlaboratory mean and median for Zinc in ampoules IADN2, IADN3, and IADN4. They had a high intercept for both metals, as did the other participants. Their results were high relative to the target for Aluminum, but they were part of the group of four laboratories that appear to demonstrate a consensus (see above and Figures 1 and 2).

Laboratory 9312 analyzed for the other six Trace Metals using Graphite Furnace - Atomic Absorption Spectroscopy (GFAAS). This technique was not sensitive enough for the lowest concentration of Arsenic and Selenium in Ampoule IADN1. They had very good agreement with the target for Selenium and a slight positive slope problem for Arsenic in Ampoule IADN4. They had very good agreement with the target and

interlaboratory mean and median for Cadmium.

Their results for Chromium and Copper were erratic, with high intercepts (Figures 7 and 9). Their Lead results indicated a negative slope problem (Figure 11). Their calibration standards should be checked with reference standards across the entire range to try and improve their performance for these three Trace Metals.

Laboratory 9313

Laboratory 9313 did not report results for Selenium. They used two different instruments for this study. For the analysis of Aluminum, Copper and Zinc, they used ICP (Table 2). They had a high intercept for all three elements, as did all of the participants in this study. They had good agreement with the target and interlaboratory mean and median for Copper and Zinc. Their results were high relative to the target for Aluminum, but they were part of the group of four laboratories that appear to demonstrate a consensus (see above and Figures 1 and 2).

Laboratory 9313 analyzed for the other four Trace Metals using Atomic Absorption Spectroscopy (AAS). They had a high intercept for Chromium and Lead, and were within approximately 10% of the target for the other three ampoules (Figures 8 and 12). They had good agreement with the target for Cadmium, except for Ampoule IADN2, where they were slightly erratic. They had a high slope bias of 10% for Arsenic.

Laboratory 9314

Laboratory 9314 had good agreement with the target and interlaboratory mean and median for Arsenic, Cadmium, Lead, and Selenium. They had a high intercept for Chromium, Copper and Zinc, but good agreement with the target and interlaboratory mean and median for the higher concentrations (Ampoules IADN2, IADN3, and IADN4). Their results were high relative to the target for Aluminum, but they were part of the group of four laboratories that appear to demonstrate a consensus (see above and Figures 1 and 2).

Laboratory 9315

Laboratory 9315 noted that their certified method does not include Chromium and Selenium, so that their results for these two Trace Metals may not be reliable. They have good agreement with the target and interlaboratory mean and median for Chromium (Figure 7), but they are biased low for Selenium (Figure 13). Development of a certified method for Selenium should help improve their results for this metal.

They had good agreement with the target and interlaboratory mean and median for Arsenic and Lead. Their results for Copper and Zinc demonstrated a high intercept and a negative slope, though they are within 5-10% of the target at the higher concentrations (Ampoules IADN3 and IADN4). Laboratory 9315 had a negative intercept for Cadmium, with a positive slope (Figure 5), though they are within 5-8% of the target (Figure 6). Their results were high relative to the target for Aluminum, but they were part of the group of four laboratories that appear to demonstrate a consensus (see above and Figures 1 and 2). Their results were the closest to the target of the group of four laboratories but they were the lowest among the group of four (Figure 1).

Laboratory 9316

Laboratory 9316 reported that all of the solutions were diluted so as to meet the minimum volume required for analysis. They were unable to report results for Arsenic and Selenium as they required unpreserved samples for analysis.

Their results for Cadmium demonstrated good agreement with the target and interlaboratory mean and median. They had a high intercept for Copper and Lead, with good agreement with the target and interlaboratory mean and median at the higher concentrations (Figures 9 and 11). Laboratory 9316 had the same high intercept bias for Zinc as the other participants (Figure 15), but they also had a positive slope problem.

Laboratory 9316 had erratic performance for Aluminum and Chromium. For Aluminum they were biased low for Ampoules IADN1, IADN2, and IADN3, but were biased very high for Ampoule IADN4 (Figure 1). Their results demonstrated the opposite pattern for Chromium (Figure 7). For both of these Trace Metals, the results had been blank corrected. The variability in these results indicates that applying a blank correction must be done with caution. It is not known if the correction factor applied was based on a "blank" sample on the day of analysis of the interlaboratory study samples, or a "mean blank" that is based on at least a month's worth of data. A single "blank" value is not as reliable as a "mean blank", as the former may have been individually contaminated, while the latter reflects conditions that occur more uniformly. Laboratory 9316 should monitor their "blank" carefully for Aluminum and Chromium, as they may be over-correcting their results.

5 CONCLUSION

The results of this interlaboratory study indicate that the participants have maintained or improved their between-laboratory variability as compared to the first interlaboratory study[4] among this group of laboratories. Individual participants may have problems with one or two of the Trace Metals, but to maintain confidentiality, individual laboratories' performance has not been directly compared for the two studies.

The target levels were lower in this study as compared to the previous study[4], so as to evaluate sensitivity at lower levels. Intercept problems were demonstrated for Aluminum, Copper, Lead, and Zinc. Improvements may not be possible due to the current state of analytical capability.

It is the intent to continue with future interlaboratory studies in support of the IADN program. As well as continuing to assess between-laboratory calibration, spiked matrix samples for air and precipitation will be used to compare between-laboratory method performance.

6 REFERENCES

1. International Joint Commission, United States and Canada; January 1988. *Revised Great Lakes Water Quality Agreement of 1978 as amended by Protocol signed November 18, 1987.*

2. Canada/U.S. Coordinating Committee on Annex 15; March 1990. *Integrated Atmospheric Deposition Network Implementation Plan.*

3. *Integrated Atmospheric Deposition Network Quality Assurance Program Plan* (DRAFT); May 19, 1993.

4. Cussion, S.; January 1994; *Interlaboratory Study 92-4, Trace Metal Standard Solutions in Support of the Integrated Atmospheric Deposition Network (IADN), July 1992.* Ontario Ministry of the Environment and Energy and Atmospheric Environment Service, Environment Canada. ISBN 0-7778-2245-8.

7   APPENDIX 1 - RESULTS AND GRAPHS

TABLE 1: INTERLABORATORY STUDY 93-1
RESULTS IN µg/L

AMPOULE	IADN1		IADN2		IADN3		IADN4	
				Al				
TARGET	Dil. Factor	25	Dil. Factor	50	Dil. Factor	100	Dil. Factor	200
9311		10 ±1		15 ±2		26 ±3	2	53 ±3
9312		56.0		97.0		144		223
9313		50.27		82.05		134.00		227.70
9314		51.6		91.0	5	150	10	246
9315		40.3		72.9		107.0		201.4
9316	2.91	14.1	2.93	13.2	2.95	48.4	2.91	274.7
MEAN		37.05		61.86		101.57		204.30
MEDIAN		45.29		77.48		120.5		225.4
STD DEV		20.07		37.89		52.47		78.09
%RSD		54.18%		61.25%		51.66%		38.22%
				As				
TARGET	Dil. Factor	0.999	Dil. Factor	2.499	Dil. Factor	29.99	Dil. Factor	74.98
9311		N/A		N/A		N/A		N/A
9312		<2.0		2.8	2	30.3	5	79.3
9313	1:2	1.095	1:5	2.730	1:20	32.844	1:29	81.200
9314		1.05		2.58		27.9		73.8
9315		1.05		2.54		27.5		72.50
9316		N/A		N/A		N/A		N/A
MEAN		1.065		2.663		29.636		76.700
MEDIAN		1.05		2.66		29.10		76.55
STD DEV		0.026		0.123		2.470		4.206
%RSD		2.44%		4.61%		8.34%		5.48%
				Cd				
TARGET	Dil. Factor	0.562	Dil. Factor	1.872	Dil. Factor	7.489	Dil. Factor	22.47
9311		0.8 ±0.5		2.4 ±0.5	5	6 ±1	5	20 ±3
9312		0.6		1.8	5	7.4	10	22.6
9313		0.604	1:5	2.316	1:10	7.579	1:2	22.575
9314		0.61		1.88		7.35		21.8
9315		0.52		1.72		6.93		23.50
9316	2.91	0.6	2.93	2.1	2.95	7.7	2.91	22.12
MEAN		0.622		2.036		7.160		22.099
MEDIAN		0.602		1.990		7.375		22.348
STD DEV		0.093		0.281		0.626		1.178
%RSD		14.99%		13.80%		8.74%		5.33%
				Cr				
TARGET	Dil. Factor	0.499	Dil. Factor	2.499	Dil. Factor	3.748	Dil. Factor	24.99
9311		<3		3 ±3		5 ±3		26 ±4
9312		1.8		3.1		3.7	5	29.5
9313	1:3	0.720	1:3	3.008	1:5	4.176	1:32	27.027
9314		0.71		2.78		3.90		24.3
9315		0.74		2.86		3.95		24.90
9316	2.91	0.6	2.93	3.6	2.95	5.7	2.91	23.6
MEAN		0.762		3.058		4.404		25.888
MEDIAN		0.730		3.004		4.063		25.450
STD DEV		0.581		0.289		0.780		2.149
%RSD		76.31%		9.45%		17.71%		8.30%

Dil. Factor = Dilution Factor
If no value is indicated in Table 1, then the Dilution Factor = 1.

TABLE 1: INTERLABORATORY STUDY 93-1
RESULTS IN µg/L

AMPOULE	IADN1		IADN2		IADN3		IADN4	
				Cu				
TARGET	Dil. Factor	1.049	Dil. Factor	5.244	Dil. Factor	26.22	Dil. Factor	52.44
9311		2 ± 2		7 ± 2		27 ± 5	5	48 ± 5
9312	2	5.5	2	6.7	20	29.8	50	52.4
9313		1.47		6.22		27.70		53.56
9314		1.40		6.29		26.6		51.6
9315		1.56		7.06		25.4		49.50
9316	2.91	1.5	2.93	6.7	2.95	28.3	2.91	51.8
MEAN		2.238		6.662		27.467		51.143
MEDIAN		1.53		6.70		27.35		51.70
STD DEV		1.612		0.349		1.512		2.032
%RSD		72.02%		5.24%		5.51%		3.97%
				Pb				
TARGET	Dil. Factor	2.499	Dil. Factor	9.994	Dil. Factor	24.99	Dil. Factor	49.97
9311		1 ± 1		8 ± 2		21 ± 2	2	45 ± 5
9312		3.6		8.9		17.0		33.0
9313		3.56	1:2	11.34	1:5	25.08	1:15	54.40
9314		2.67		9.99		24.4		48.8
9315		3.09		10.7		25.6		49.80
9316	2.91	3.8	2.93	10.5	2.95	26.6	2.91	50.9
MEAN		2.953		9.905		23.280		46.983
MEDIAN		3.33		10.25		24.74		49.30
STD DEV		1.041		1.240		3.620		7.497
%RSD		35.25%		12.52%		15.55%		15.96%
				Se				
TARGET	Dil. Factor	1.003	Dil. Factor	3.008	Dil. Factor	30.08	Dil. Factor	80.2
9311		N/A		N/A		N/A		N/A
9312		<2.0		3.2	2	30.0	5	80.5
9313		N/A		N/A		N/A		N/A
9314		1.01		3.12		29.9		79.2
9315		0.96		2.57		27.3		74.7
9316		N/A		N/A		N/A		N/A
MEAN		0.985		2.963		29.067		78.133
MEDIAN		1.01		3.12		29.90		79.20
STD DEV		0.035		0.343		1.531		3.044
%RSD		3.59%		11.57%		5.27%		3.90%
				Zn				
TARGET	Dil. Factor	4.00	Dil. Factor	1.00	Dil. Factor	50.0	Dil. Factor	80.0
9311		7 ± 3		4 ± 3		40 ± 5		50 ± 5
9312		7.0		3.0		51.0		82.0
9313		6.77		5.51		50.28		83.36
9314		5.68		2.62		50.8		81.6
9315		6.90		2.38		45.9		72.90
9316	2.91	6.7	2.93	3.2	2.95	54.0	2.91	96.0
MEAN		6.675		3.452		48.663		77.643
MEDIAN		6.84		3.10		50.54		81.80
STD DEV		0.502		1.153		4.976		15.433
%RSD		7.53%		33.40%		10.23%		19.88%

Dil. Factor = Dilution Factor
If no value is indicated in Table 1, then the Dilution Factor = 1.

TABLE 2: INSTRUMENTATION FOR INTERLABORATORY STUDY 93-1

PARTICIPANT	INSTRUMENTATION
9311	Perkin-Elmer AAS Model 305 and Graphite Furnace Model HGA-74
9312	Al, Zn: ICP-AES As, Cd, Cr, Cu, Pb, Se: GFAAS
9313	Al, Cu, Zn: ICP As, Cd, Cr, Pb: AAS
9314	ICP-MS
9315	ICP-MS
9316	ICP

Legend

AAS	Atomic Absorption Spectrophotometer
GFAAS	Graphite Furnace Atomic Absorption Spectrophotometer
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma - Absorption Emission Spectrophotometer
ICP-MS	Inductively Coupled Plasma - Mass Spectrometer
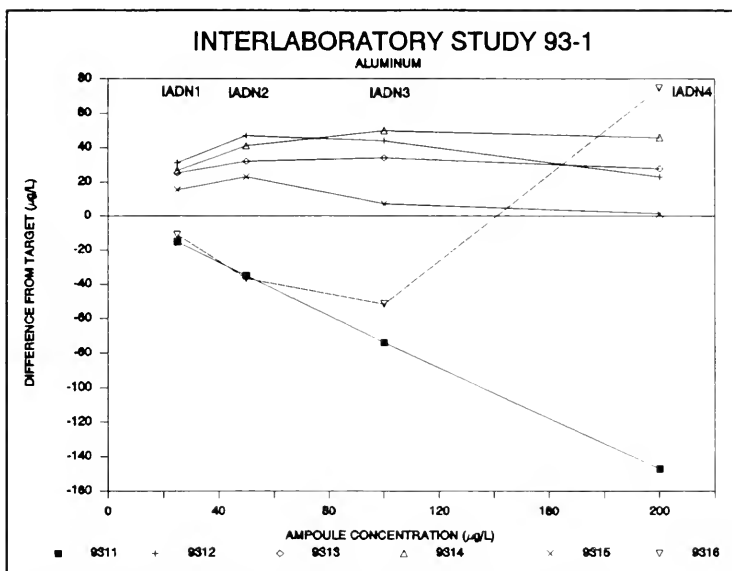
Figure 1 - Absolute Difference from Target: Aluminum
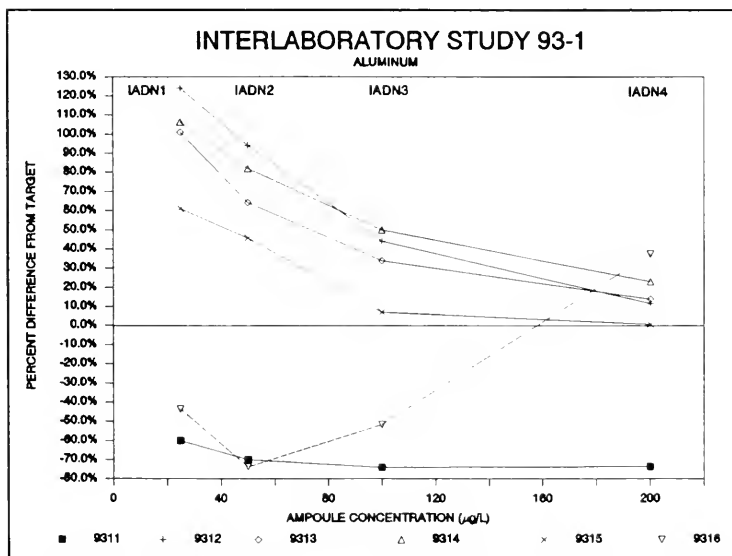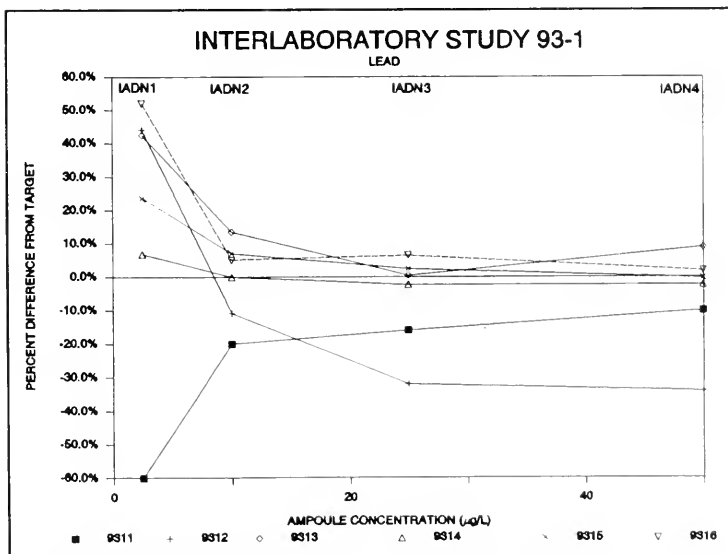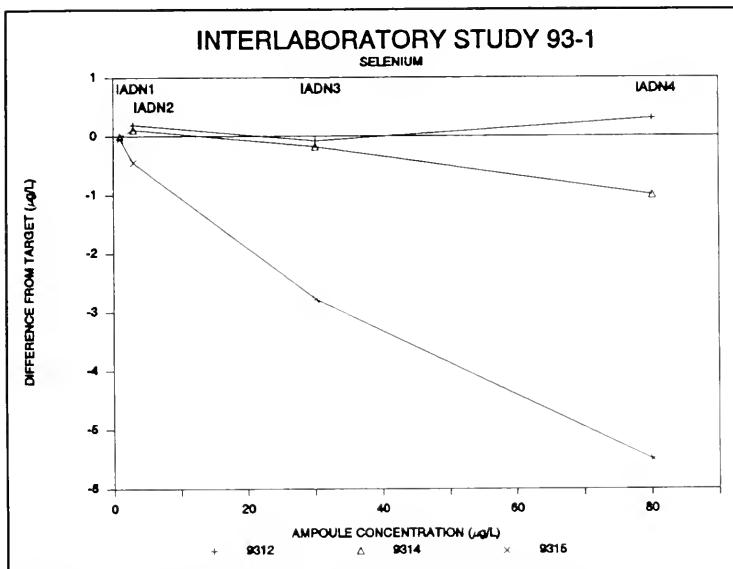

Figure 2 - Percent Difference from Target: Aluminum
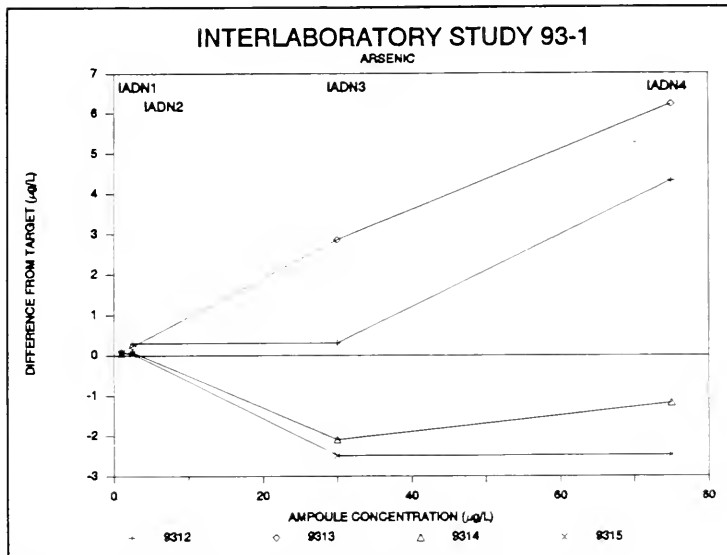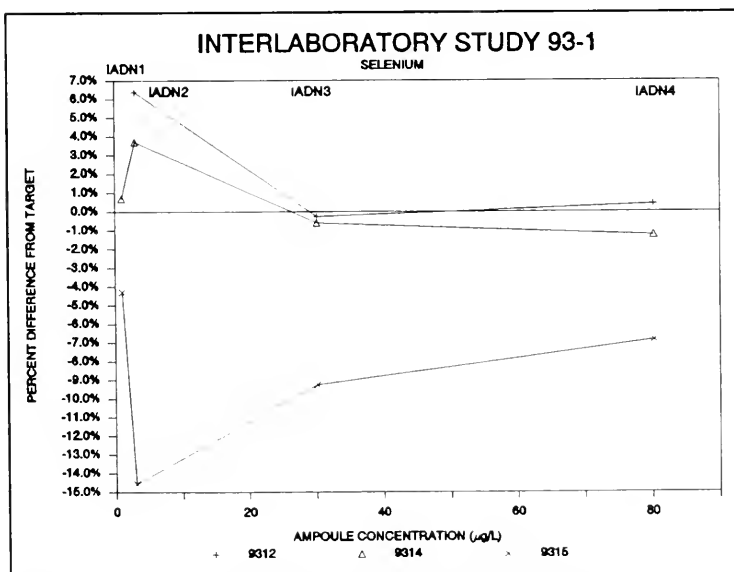
Figure 3 - Absolute Difference from Target: Arsenic
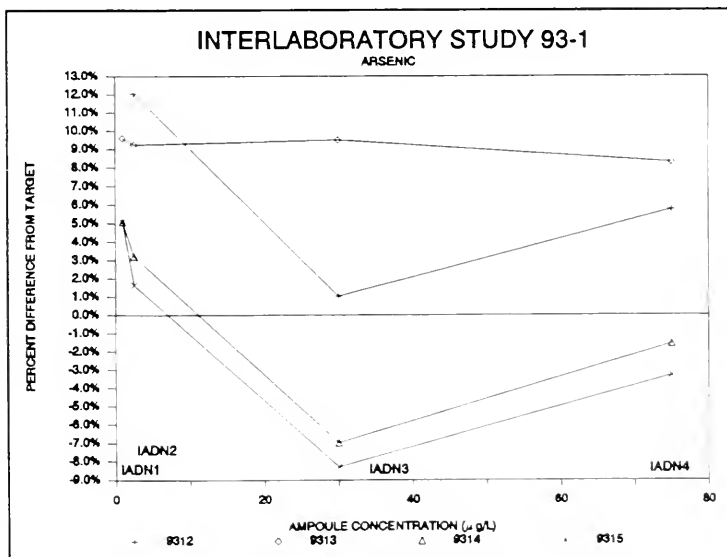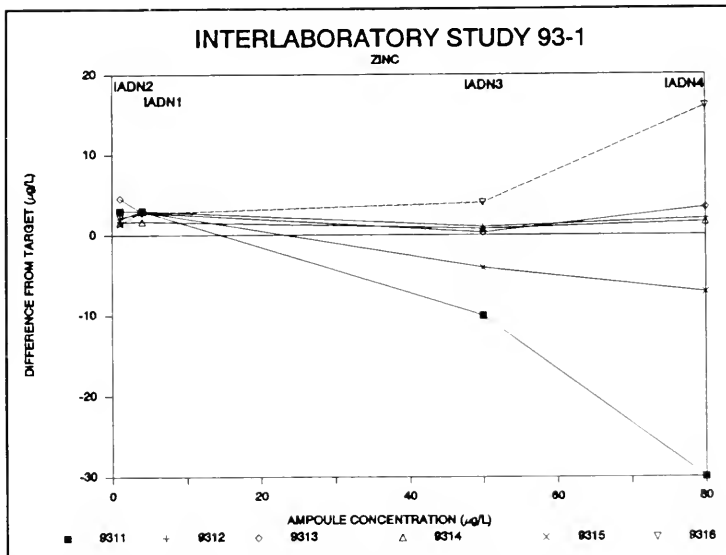

Figure 4 - Percent Difference from Target: Arsenic
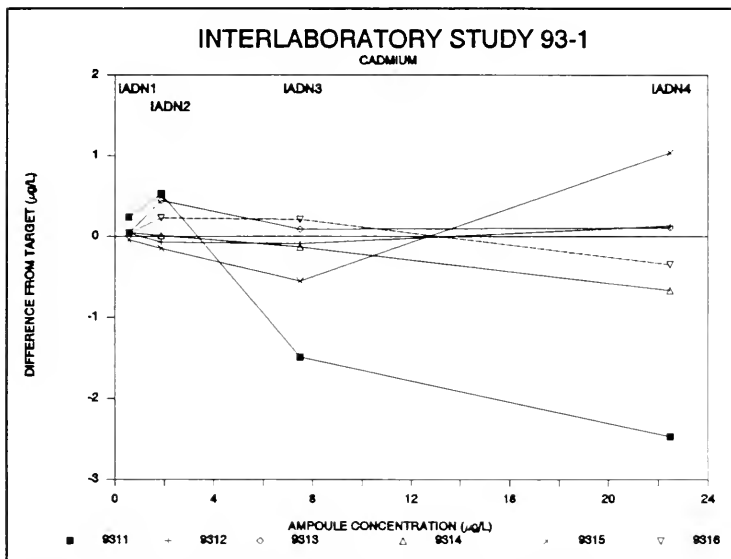
Figure 5 - Absolute Difference from Target: Cadmium
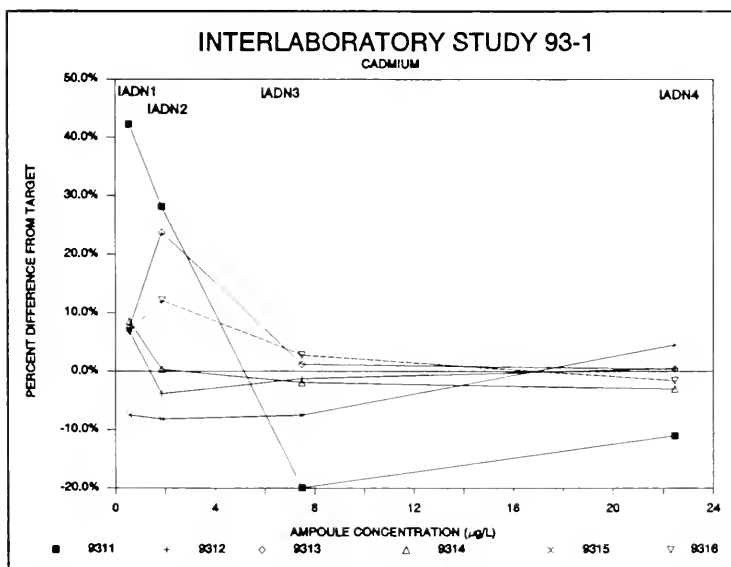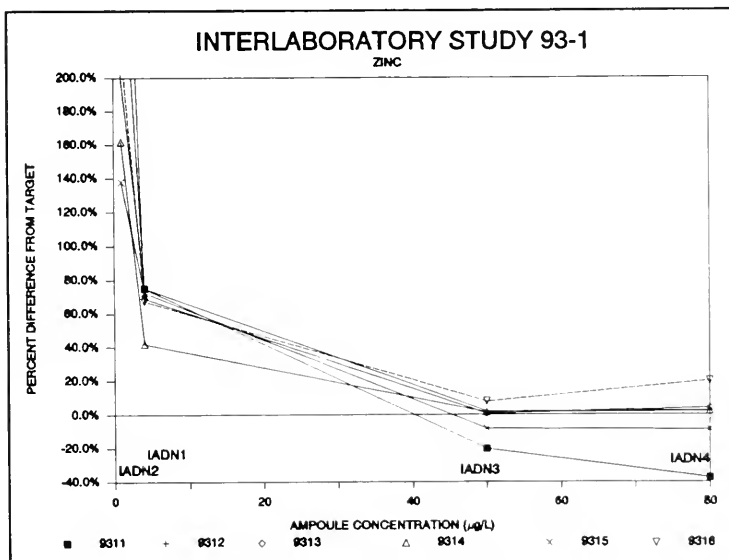

Figure 6 - Percent Difference from Target: Cadmium
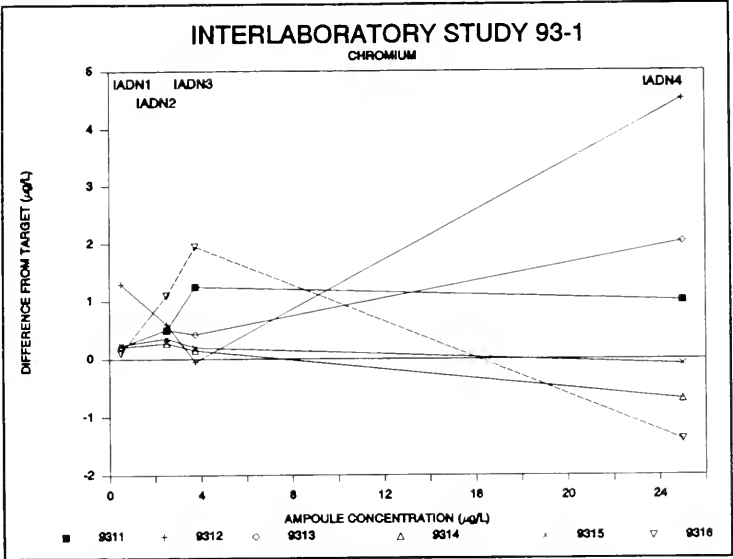
Figure 7 - Absolute Difference from Target: Chromium
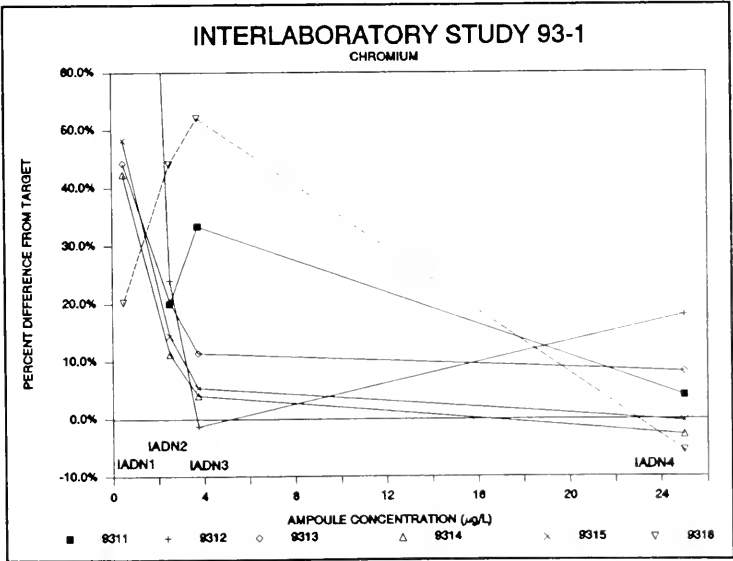
Figure 8 - Percent Difference from Target: Chromium
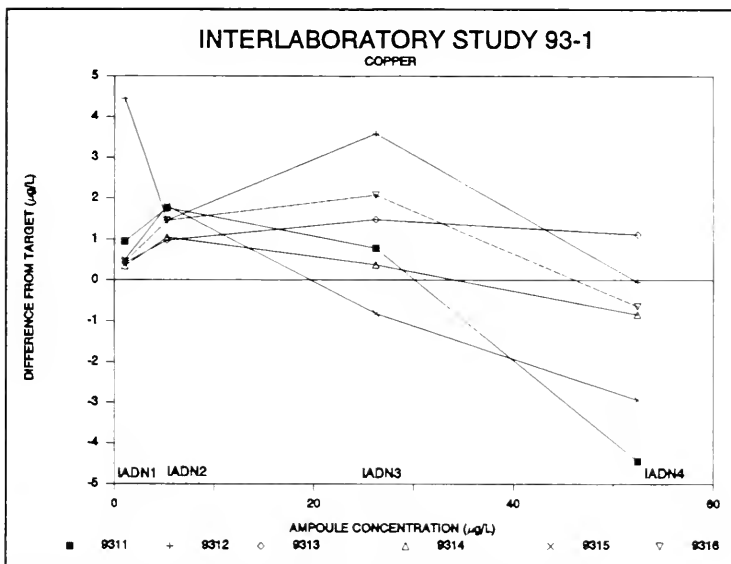
Figure 9 - Absolute Difference from Target: Copper
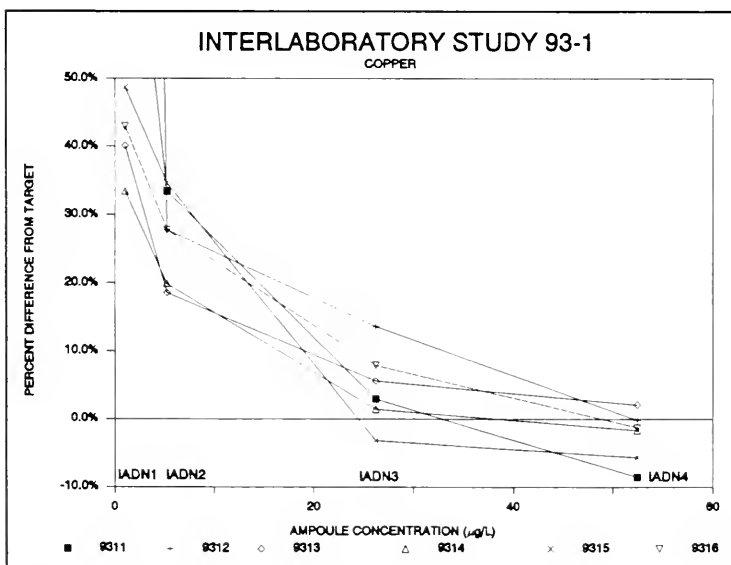
Figure 10 - Percent Difference from Target: Copper
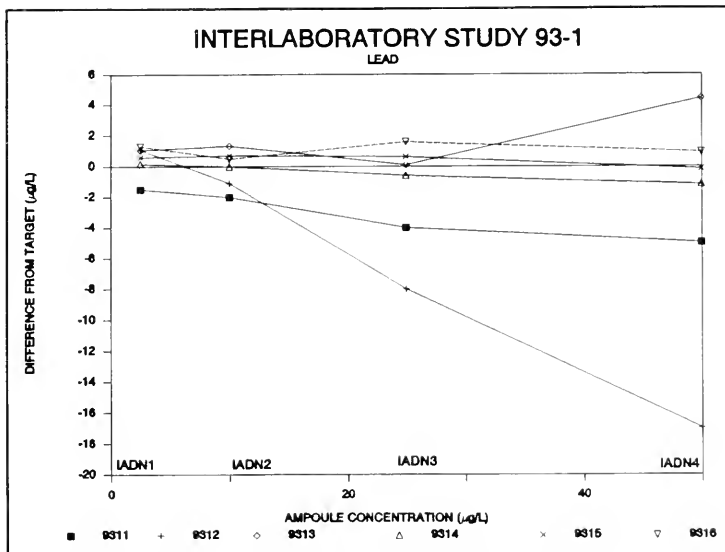
Figure 11 - Absolute Difference from Target: Lead

Figure 12 - Percent Difference from Target: Lead

Figure 13 - Absolute difference from Target: Selenium

Figure 14 - Percent Difference from Target: Selenium

Figure 15 - Absolute Difference from Target: Zinc

Figure 16 - Percent Difference from Target: Zinc

8   APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

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ARQP
4905 Dufferin St.
Downsview, Ontario
M3H 5T4
(416) 739-4847

July 13, 1993

Dear Interlaboratory Study 93-1 Participant,

Please find enclosed four 50 mL ampoules for the analysis of Trace Metals. The ampoules
are labelled IADN1, IADN2, IADN3, and IADN4. If you are missing any of the ampoules or
they have broken in transit, please contact Sathi Selliah at (416) 235-5700 immediately for
replacement.

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the
scored mark and transfer the contents to the appropriate sample container for your analytical
system. No dilutions should be required, but if you do so, please mark the dilution factor used
on the accompanying report form. All the ampoules contain the following metals: Aluminum,
Chromium, Copper, Zinc, Arsenic, Selenium, Cadmium and Lead. All solutions are preserved
with 2% nitric acid.

Please report all results on the accompanying form by August 27, 1993.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Air Toxics Quality Assurance Officer
(416) 739-4847
FAX (416) 739-5708

INTERLABORATORY STUDY 93-1

METALS FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

Element	IADN 1		IADN 2		IADN 3		IADN4	
	Dil. Factor	Result	Dil. Factor	Result	Dil. Factor	Result	Dil. Factor	Result
Al								
As								
Cd								
Cr								
Cu								
Pb								
Se								
Zn								

Dil. Factor = Dilution Factor

INSTRUMENT USED FOR ANALYSIS:

ARQP
4905 Dufferin St.
Downsview, Ontario
M3H 5T4
(416) 739-4847

October 4, 1993

Dear Participant of Interlaboratory Study 93-1,

Please find enclosed the table of results from Interlaboratory Study 93-1. If there are any transcription errors, please contact me at (416) 739-4847 by October 15, 1993.

A final report will be provided to all participants.

Your identification code is:

Sincerely,

Sylvia Cussion
Air Toxics Quality Assurance Officer
(416) 739-4847

9   APPENDIX 3 - INTERPRETATION OF BIASES IN DIFFERENCE PLOTS

Interlaboratory study results may be evaluated by comparing the difference from target (D) to the target or consensus value (X). This may be graphically represented with the Difference (D) on the vertical axis and the Target or consensus value (X) on the horizontal axis. By joining the individual points for each participant in order of increasing concentration, imprecision (squiggle in the line) versus bias or curvature (location of line relative to its expected position) may be demonstrated.

The precision envelope for the difference plots may be described by the following equation:

$$D = B_i + B_s*C \pm (DL + f*C)$$

where:

D	Difference from target		B_i	Intercept Bias
C	Concentration		B_s	Slope Bias
DL	Detection Limit		f	Fluctuation factor

The fluctuation factor (f) for Trace Metals is usually 5-10%. Data users' needs may determine how large a value for f is acceptable.

If there are no biases present (B_i and B_s = 0), the shape is symmetrical to and centred on the target line. Measurement differences among participating laboratories in an interlaboratory study should be attributable only to random fluctuation. An example using DL = 5 μg/L and f = 10% is given in Figure 17.

When an intercept bias is present, the envelope shifts in the direction of the bias. If this shift exceeds the Method Detection Limit (MDL), this becomes a matter of concern for the analyst. An example with B_i = -5 μg/L is given in Figure 19.

When a slope bias is present, the envelope broadens in the direction of the bias as concentration increases. When this bias exceeds the MDL + 10% concentration, it becomes a matter of concern for the analyst. An example of B_s = +10% is given in Figure 21.

Most interlaboratory study data sets will show a combination of slope and intercept biases among the participants. The precision envelope changes according the magnitude of both effects. An example using B_i = -5 μg/L and B_s = +10% is given in Figure 23.

The results may also plotted using the relative difference (R) on the vertical axis. the precision envelope flares dramatically as the concentration approaches zero. This type of plot tends towards an exaggerated impression of acceptable variability at the bottom end and may mask biases at higher concentration levels. However it can be useful when describing the range of performance among a group of participants. The above examples that were presented using concentration units (absolute scale) are also presented using a relative scale (Figures 18, 20, 22 and 24).

REFERENCE

King, D.E.; July 1993; *Interpretation of Interlaboratory Comparison (Round-Robin) Data*; Internal Report, Ministry of Environment and Energy, Laboratory Services Branch; Draft.
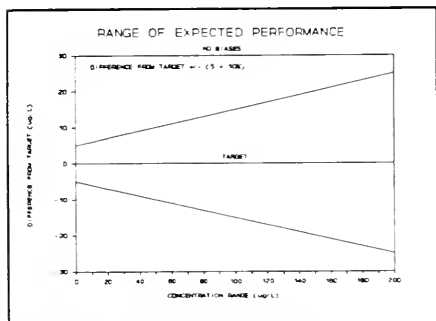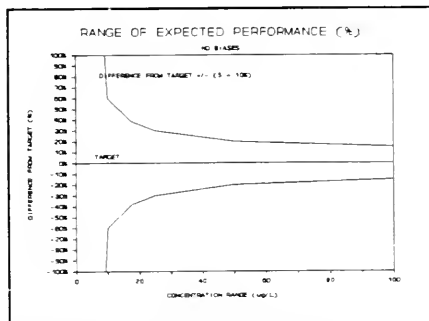

Figure 17 - Absolute Scale
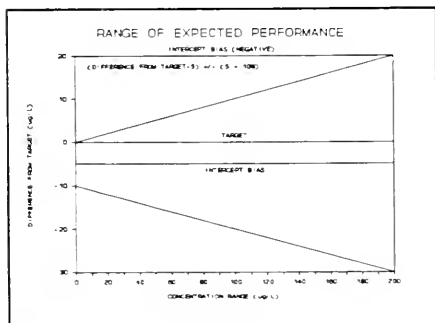

Figure 18 - Relative (%) Scale
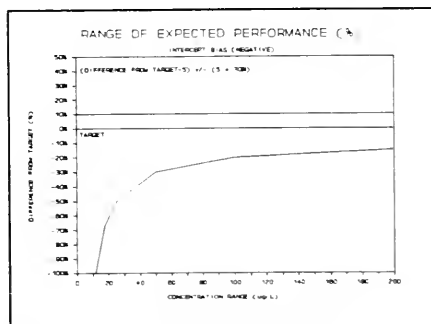

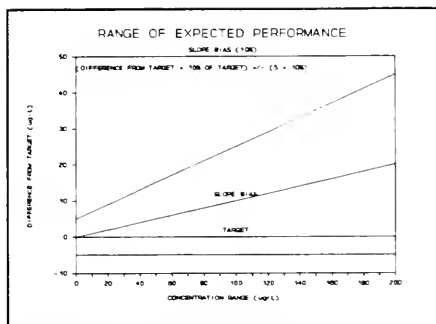Figure 19 - Absolute Scale

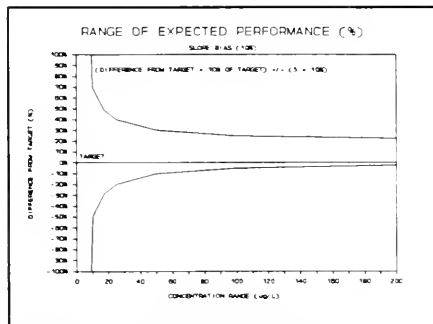Figure 20 - Relative (%) Scale

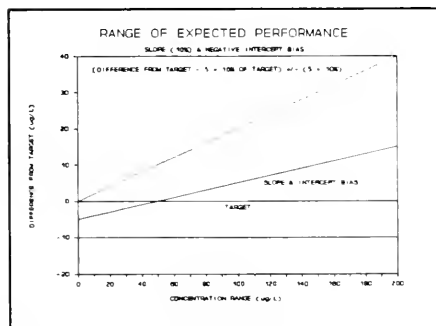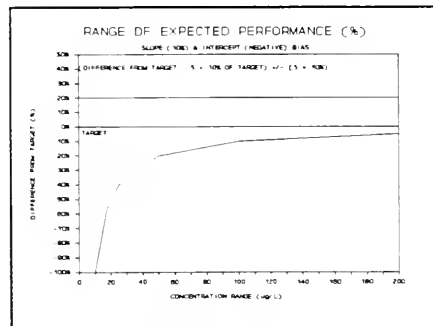Figure 21 - Absolute Scale

Figure 22 - Relative (%) Scale

Figure 23 - Absolute Scale

Figure 24 - Relative (%) Scale